

Study of the Optical Properties for ZnS Thin Film Irradiated by CO₂ Laser

A. S.Jassim ,N. A.Dahham, M.Sh.Marie

Department of Physics, College of Science , University of Tikrit

Abstract

In this study ZnS thin film was prepared by using thermal evaporation vacuum technique under the pressure (10^{-6}) Torr on glass substrate at room temperature and annealing at 523 K. Samples were irradiated to CO₂ laser of power (1 watt) and wave length (10.6) μm at distance 10 cm from the source during (5 sec). The absorbance spectra was recorded by using UV-visible spectrophotometer and used to calculate some of optical properties investigated including their transmittance, reflectance spectra, energy gap, and extinction coefficient. From the result of thin films samples at room temperature and at 523 K, we conclude that the irradiation by laser causes a decrease in the transmittance and increasing in reflection and extinction coefficient and the irradiation leads to an increase in energy gap.

Introduction

The thin film technique is one of important methods which is interested in the development and study of semiconductor material.

The study of material properties lead to draw attention physicians toward this technique, from the second half of seventeenth century, many of researches were taken out in the field [1, 2]. In the nineteenth century there has been an improvement in the experimental part of thin film [3, 4]. The thin film is one layer or many layers for specific material in the range of tens nanometers thickness in some of micrometers [5].

Metal chalcogenides (sulfides, tellurides and Selenides) are of great importance for research because they are potential candidates for optoelectronic application such as photo detectors, solar cells, and thin film transistors etc [6].

Zinc Sulphide is an important II-VI group semiconductor with a large direct energy gap of (3.50-3.70) eV in the UV range, direct energy gap $E_g = 3.68$ eV for bulk ZnS [7]. It is used as a key material for light emitting diodes and other optoelectronic devices such as electroluminescent displays, Cathodoluminescent displays and multilayer dielectric filters. ZnS is highly suitable as a window layer in heterojunction photovoltaic solar cells; because the wide band decreases the window absorption losses and improves the short circuit current of the cell. In the area of optics, ZnS can be used as a reflector, because of its high refractive index (2.35), and a dielectric filter because of its high transmittance, in the visible range [7, 8, and 9].

ZnS was studied by M.Y. Nadeem and W. Ahmed. They found that ZnS thin films grown here have energy gap in the range (3.51 -3.84) eV and found that the refractive index increased for prepared thin film [10]. J.P. Borah and K.C. Sarma found that ZnS nanocrystalline films grown on glass substrates using PVA as matrix, also found that thin films would be photosensitive. The films kept in air adsorb oxygen from air and they found that their resistance increases as observed from I/V characteristics. SEM study indicated a nanoparticle formation in thin film [9]. Vipin Kuma, M.K. Sharm, J. Gau and T. P.Sharm show that the energy gap of ZnS sintered film comes out to be 3.50 eV. The films of ZnS are found to be polycrystalline in nature and have hexagonal wurtzite structure. It has been observed that the electrical resistivity

and activation energy of ZnS comes out to be 0.370×10^5 ohm cm and 0.80 eV respectively. The conduction in ZnS film is through thermally activated process [7].

Among molecular lasers, the CO₂ laser is of greatest practical importance. The high level of efficiency with laser in which laser radiation can be generated in continuous wave (CW) and pulse operation is its most fascinating feature. In atom and ion lasers, laser radiation is the result of the electron transitions close to the limit for single or double ionization. The infrared radiation of the CO₂ laser on the other hands is the result of the energy exchange between rotational-vibrational levels within the electron ground level [11].

The objective of this research is to study the behavior of the material (ZnS) before the effect of laser radiation and what happen after irradiation by CO₂ laser

Experimental and theoretical part

ZnS thin film was prepared by using thermal evaporation vacuum technique under the pressure (10^{-6}) Torr on glass substrate at room temperature. Thickness of the films has been carried out by weighting method and the measured thicknesses were about (300 nm) then the films were annealed at 523K by using electric oven. Samples were irradiated to CO₂ laser of power (1 watt) and wave length (10.6 μm) at distance (10 cm) from the source during (5 sec). The absorbance ad transmission spectra were recorded using uv-visible spectrophotometer type centra-5 in the range of wave length (180-1100) nm at room temperature .Some of optical properties was calculated from absorbance and transmittance spectra. The transmittance (T) was calculated from the relation[12]:

$$T = \text{Log } 1/A \dots\dots\dots (1)$$

Where A is the absorbance. The reflection from the surface of the prepared thin films was calculated from the relation [12]:

$$R = 1 - A - T \dots\dots\dots (2)$$

The extinction coefficient K_0 was calculated from the relation [13]:

$$K_0 = \alpha \lambda / 4\pi \dots\dots\dots (3)$$

Where λ is the wave length and α is absorption coefficient. The relation between the absorption coefficient and photon energy $h\nu$ is given by [14]:

$$\alpha h\nu = A (h\nu - E_g \pm E_p)^n \dots\dots\dots (4)$$

Where E_p is photon energy and E_g is the energy gap in a direct transition and (n) is equal to 1/2.

Results and Discussion

1. Transmittance

The plot of transmission data versus wave length (μm) is shown in figure (1). We can see the maximum value for transmission at room temperature before irradiation with CO₂ laser is 0.999% at wave length 0.184 μm that means at (UV) and the maximum value for transmission after irradiation with laser is 0.998% at the wave length 0.4 μm (*visible region*) as shown in figure (2), so we can note the transmission is *decreasing* after irradiation with laser because laser causes to rearrange the atoms.

Figure (3) represents the transmittance as a function to wave length (μm) with annealing at 523K *before* irradiation with laser, so we note the maximum value of transmission is 0.9997% at the wave length 0.4 μm. We note a small increase in value of transmission before and after annealing, the maximum value in transmittance happened in visible region, while figure (4) represents the transmission as a function to wave length (μm) with annealing at 523 K after irradiation with laser and the maximum value for transmittance is 0.9999 % at the wave length 0.488 (μm). So we can note an increase in the transmittance value and shifting in wave length

because laser causes crystal defect in the sample after irradiation ,this defect causes to increase the localized electronic states which increasing the absorption and decreases the transmission .

(2) Reflectance

Figure (5) shows a plot of reflectance against wave length (μm) it can be noticed that the maximum value of reflectance before irradiation with laser at room temperature is 0.033% at the wave length 0.304 μm and after irradiation the maximum value is 0.058 % at the wave length 0.304 (μm) as shown in figure (6). And we note an increase at reflection after irradiation .We can explain this increase in the reflectance value because some of sub levels appeared in the crystal lattice for *ZnS* lattice.

Figure (7) shows the reflectance as a function to wave length (μm) with annealing in 250 °C before irradiation with CO₂ laser. In this plot we note the maximum value for reflectance is 0.0168 % at the wave length 0.296 (μm) and figure (8) represents the reflectance as a function to wave length (μm) and the maximum value is 0.0137 % at the wave length 0.296 (μm), that is means the reflectance is decreasing after irradiation with laser .This decrease may be happened because the transmittance was increased.

3 .Extinction Coefficient

Figure (9) shows the behavior of the extinction coefficient versus wave length (μm). It can be noticed that the maximum value for extinction coefficient before irradiation with laser is 0.000166 at the wave length 0.304 (μm) and after irradiation the maximum value for extinction coefficient is 0.00031 at the same wave length 0.304 (μm) as shown in figure (10) .This increasing was happened because the absorption was increasing and the relation between the absorption coefficient and extinction coefficient is linear.

Figure (11) shows the extinction coefficient as a function of wave length (μm) with annealing 250 °C before irradiation with laser the maximum value is $7.97 \cdot 10^{-5}$ at the wave length 0.296 (μm), and figure (12) represents to the extinction coefficient as a function of wave length (μm) with annealing in 250 °C after irradiation with laser and the maximum value is $6.47 \cdot 10^{-5}$ at the wave length 0.296 (μm). And we note the value for extinction coefficient is decreasing after irradiation with laser because the relation between the absorption coefficient and extinction coefficient is linear.

4. Energy gap

a plot of $(\alpha h\nu)^2$ as a function of photo energy is show in figure (13) which represents the direct optical forbidden energy gap to allow direct electronic transmission at room temperature before irradiation with laser and the value of this gap is 3.45 eV, and figure (14) represents the direct optical forbidden energy gap to allow direct electronic transmission at room temperature after irradiation with laser and the value of this gap is 3.62 eV. This result coherent with theoretical direct energy gap[7] . We note the increase in energy gap value this increase in gap may be happened because some of crystal defects were appeared in crystal lattice after irradiation with laser. These defect caused the increase of the density of localize states in the E_g .

Figure (15) shaws the relation between $(\alpha h\nu)^2$ as a function of photon energy from this relation we calculated the value of energy gap in (eV) with annealing in 250 °C before irradiation with laser which equals to 4 eV. And figure (16) represents the relation between $(\alpha h\nu)^2$ as a function of photon energy from this relation we calculated the value of energy gap in (eV) with annealing in 250 °C after irradiation with laser which equals to 4.15 (eV), this increase in energy gap may happen in result because some of crystal defects appeared in crystal lattice after irradiation with laser for the same reasons we mentioned before.

Conclusion

1. Irradiation with CO_2 laser leads to a decrease in the transmittance
2. Reflectance and extinction coefficient increase after irradiation with laser, which means the absorption is not attributed to the free carriers only, but to defect or localized electronic states
3. The laser radiation causes the increase in energy gap.

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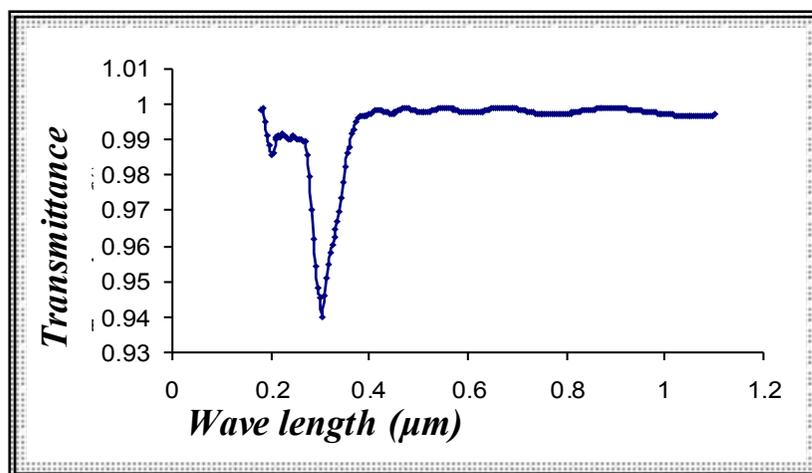


Fig.(1) transmittance as a function to wave length at room temperature before irradiation

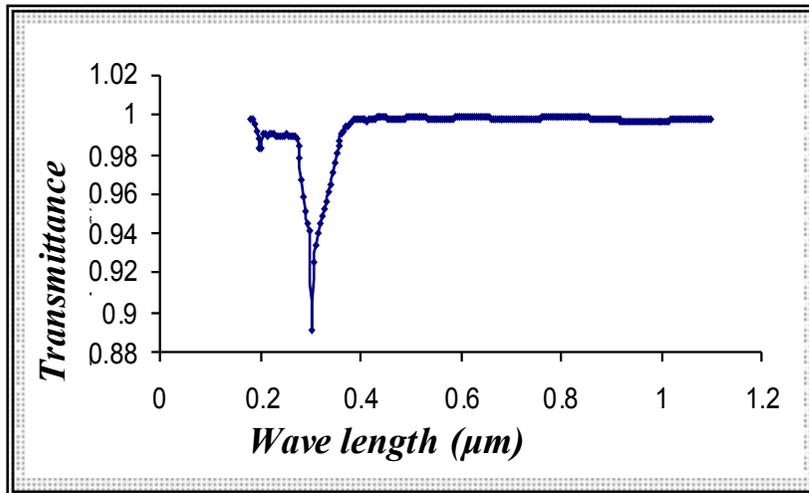


Fig.(2) transmittance as a function to wave length at room temperature after irradiation

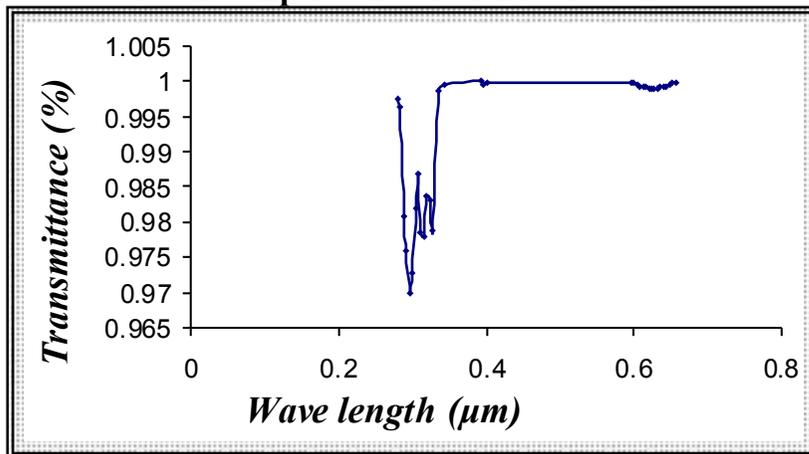


Fig.(3) transmittance as a function to wave length at room temperature after irradiation

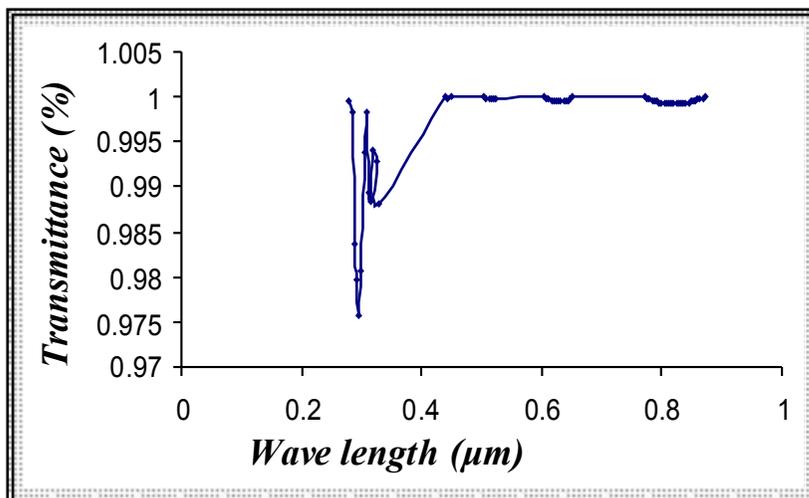


Fig.(4) transmittance as a function to wave length at room temperature after irradiation

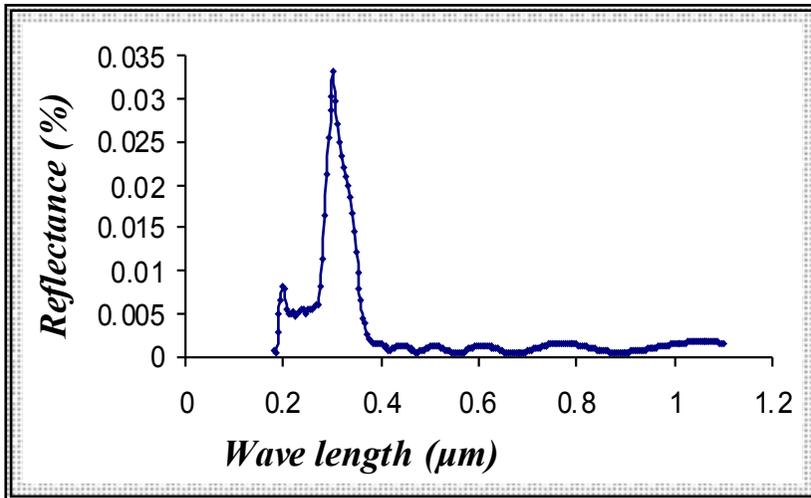


Fig.(5) Reflectance as a function to wave length at room temperature before irradiation

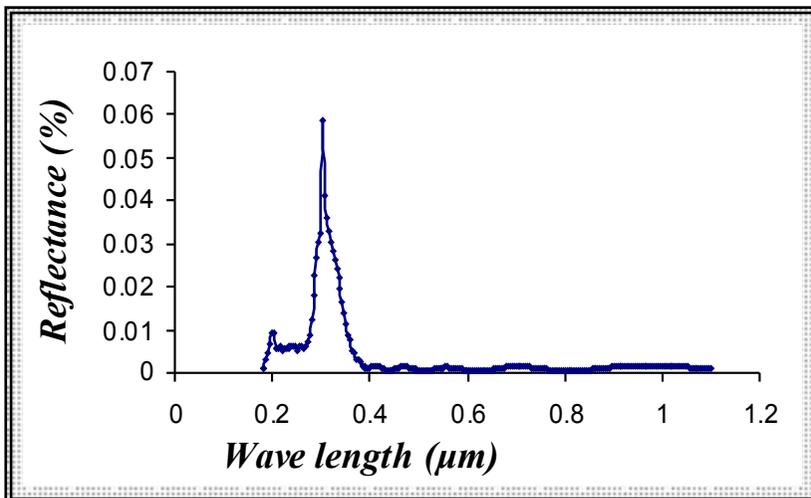


Fig.(6) Reflectance as a function to wave length at room temperature after irradiation

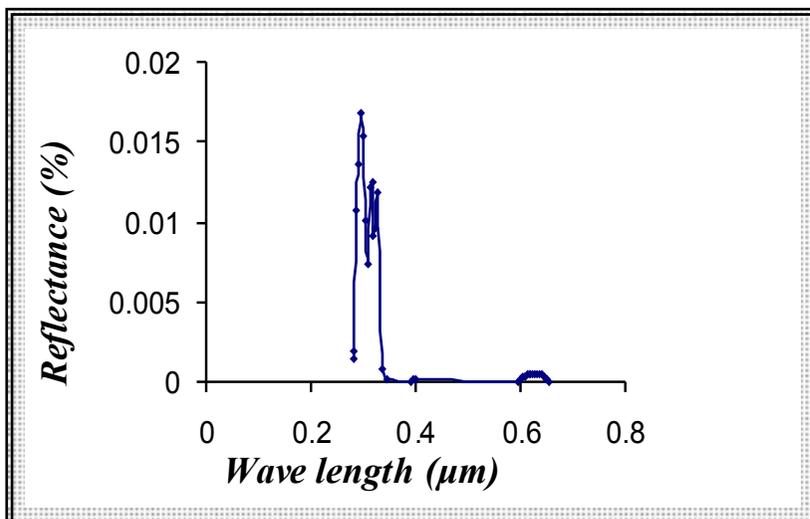


Fig.(7) Reflectance as a function to wave length at 523 K before irradiation

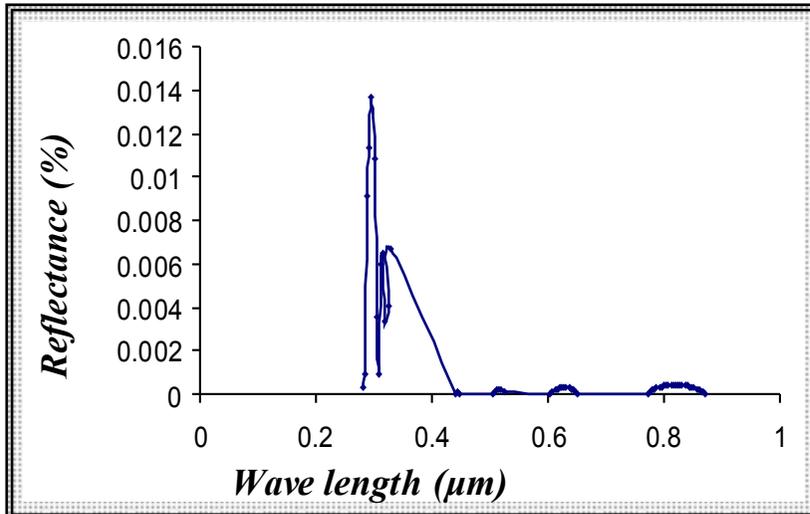
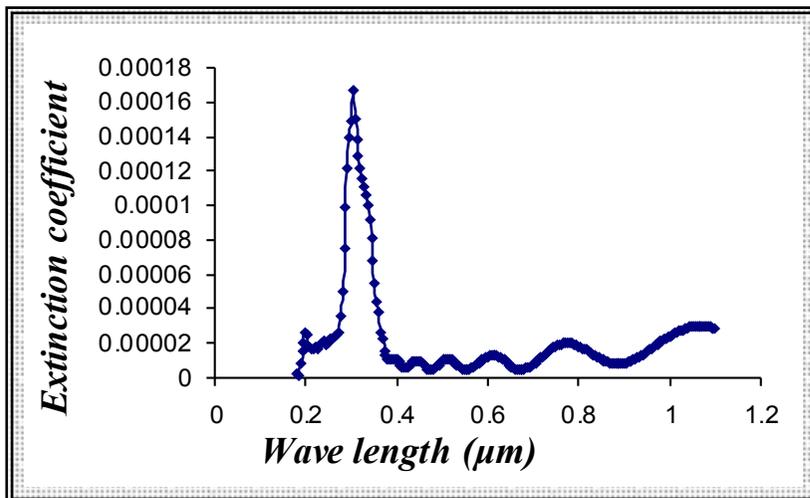


Fig.(8) Reflectance as a function to wave length at 523 K after irradiation



Fig(9) Extinction coefficient as a function to wave length at room temperature before irradiation

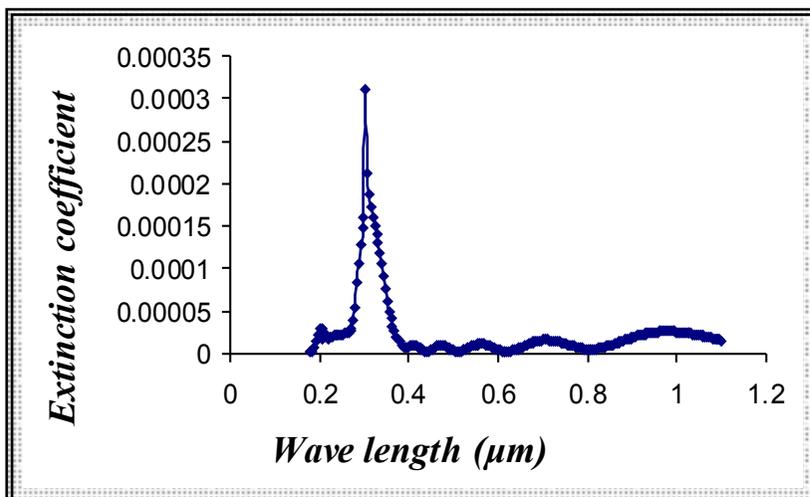


Fig.(10) Extinction coefficient as a function to wave length at room temperature after irradiation

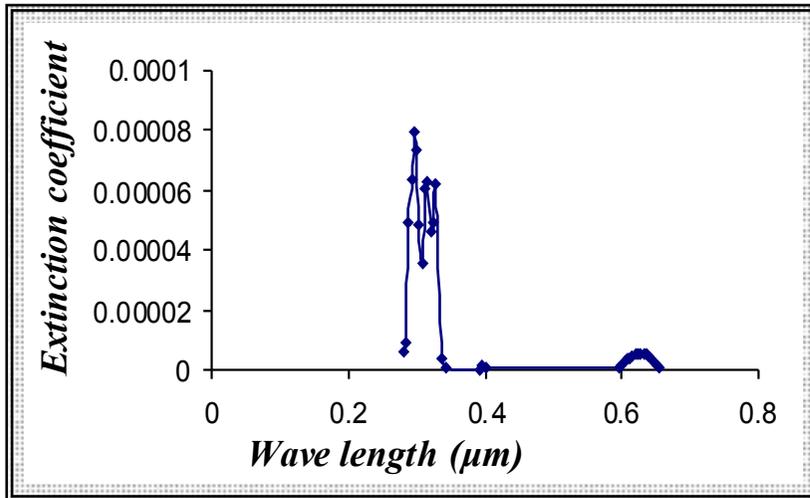


Fig.(11) Extinction coefficient as a function to wave length at 523 K before irradiation

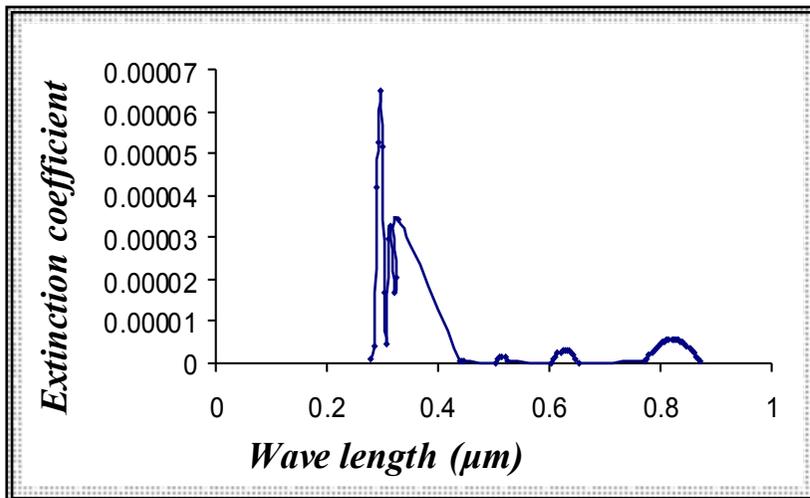


Fig.(12) Extinction coefficient as a function to wave length at 523 K after irradiation

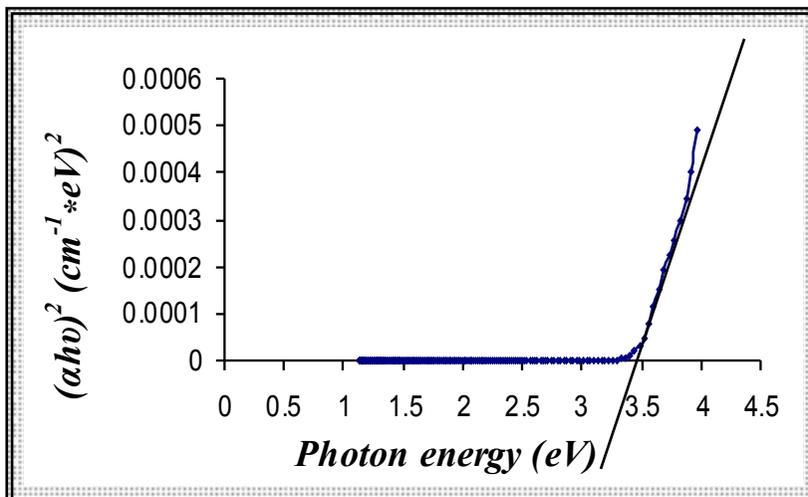


Fig.(13) Optical forbidden energy gap for direct electronic transmission at room temperature before irradiation with laser

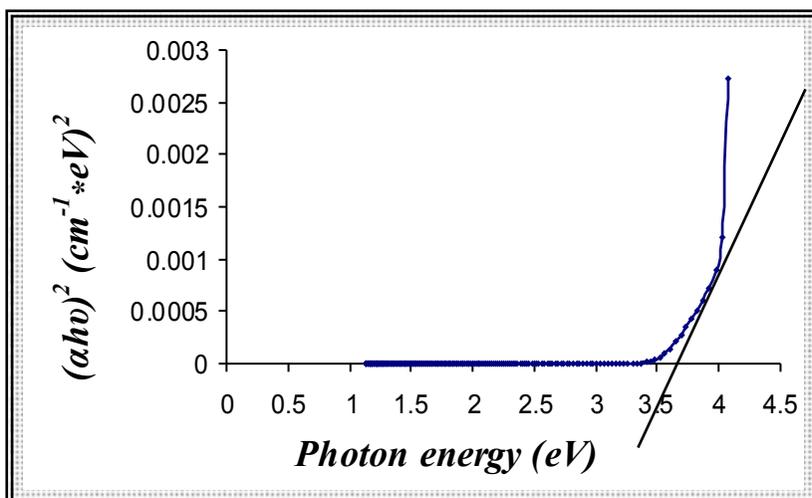


Fig.(14) Optical forbidden energy gap for direct electronic transmission at room temperature after irradiation with laser

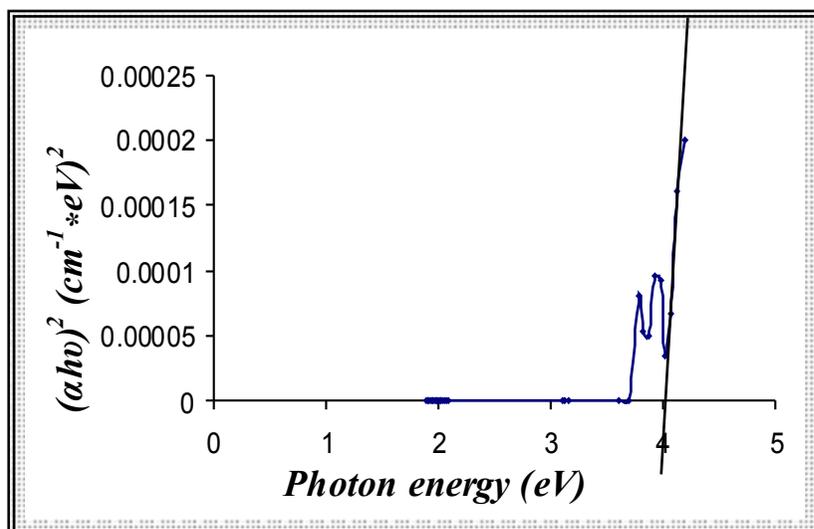


Fig.(15) Optical forbidden energy gap for direct electronic transmission at 523 K before irradiation with laser

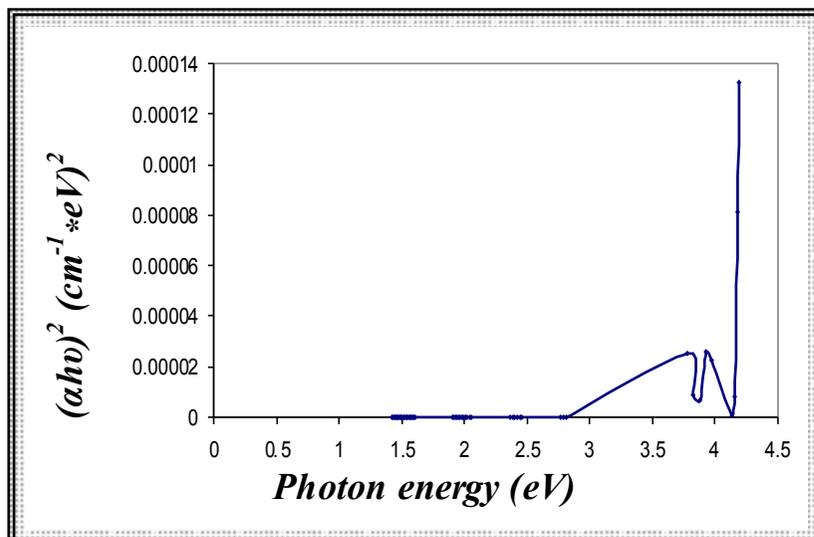


Fig. (16) Optical forbidden energy gap for direct electronic transmission at 523 K after irradiation with laser

دراسة الخواص البصرية لغشاء ZnS المشع بليزر CO₂

عواطف صابر جاسم ، نجاة احمد دحام ، محمد شياع مرعي
قسم الفيزياء، كلية العلوم، جامعة تكريت

الخلاصة

تم في هذه الدراسة تحضير اغشية رقيقة من مادة ZnS والمحضرة بطريقة التبخير الحراري الفراغي تحت ضغط (10^{-6}) على قواعد من الزجاج في درجة حرارة الغرفة، وتم تليدين العينات بدرجة حرارة (523 K) وتم تشعيع العينات بليزر CO₂ ذي طاقة (1watt) وطول موجي (10.6 μ m) وعلى بعد (10Cm) من المصدر. ومدة (5 sec) وسجل طيف الامتصاصيه باستخدام مطياف UV-visible ومنه حسبت بعض الخواص البصريه التي تتضمن النفاذية والانعكاسية ومعامل الخمود وفجوة الطاقة . ومن نتائج نماذج الاغشية الرقيقة المحضرة بدرجة حرارة الغرفة والملدنة بدرجة (523 K) والمشععة بليزر CO₂ استنتج ان التشعيع بالليزر ادى الى نقصان في النفاذيه وزياده في الامتصاصيه ومعامل الخمود وكذلك التشعيع ادى الى زيادة في فجوة الطاقة.